

**POLYNUCLEAR AROMATIC HYDROCARBONS
IN
SOLID MATRICES**

PERFORMANCE ASSESSMENT PROGRAM

A REPORT ON INTERLABORATORY STUDY 98-2

OCTOBER 1999

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1 EXECUTIVE SUMMARY

A Performance Assessment Program in the form of an interlaboratory study was offered to interested participants of the training program for Polynuclear Aromatic Hydrocarbons (PAH) in solid matrices conducted by the Laboratory Services Branch (LSB) of the Ontario Ministry of the Environment (MOE). Eight laboratories from the training program agreed to participate. Three other laboratories were invited to participate in this study.

The study was designed primarily to assess method performance including instrument calibration. Each laboratory was provided an injection ready standard and two solid materials for analysis.

The study demonstrated that:

1. The overall uncertainty of the analytical data is high.

This finding, though not surprising, is relevant when explaining differences in data sets produced by two or more laboratories.

A) Most laboratories had problems with their calibration standards.

It is clear that most laboratories must validate their standards on frequent intervals. Use of internationally accepted certified reference standards for validation is strongly recommended.

B) Most laboratories though capable of precise analysis, are experiencing some systematic problems in the analysis of solid materials. These systematic problems are possibly caused by inadequacies of the extraction procedure and/or the calibration problems identified earlier.

The use of suitable reference materials on a continuous basis to monitor sample clean-up/extraction efficiency, is recommended to ensure the production of good quality data. Even though surrogates were used, no laboratory made corrections for surrogate recoveries. Corrections for surrogate recovery may be another step towards the improvement of data quality.

2. Given the observed uncertainty of the PAH analysis, the distribution of the results for the candidate Reference Material LSBRM9801 is very heartening.

The results of this study have shown that this material contains PAH's at levels close to the MDL's suggested in the Ministry's "Guidance on Sampling and Analytical Methods for use at Contaminated Sites in Ontario". It should be very valuable as a QC Reference Material to monitor the performance of the method, particularly at low concentration levels.

3. Individual laboratory performance varied widely.

The performance of Laboratory 98206 is outstanding. All parameters of the injection standards were within 20% of the study mean and in the analysis of the reference material MOE-PTSEC2, no parameter deviated from the certified value by more than two standard deviations.

Second to Laboratory 98206 is Laboratory 98208. All parameters of the injection standards were within 20% of the study mean and only one parameter in the analysis of the reference material MOE-PTSEC2, deviated from the certified value by more than two standard deviations.

Performance of the laboratories are tabulated in the ascending order of outliers. An outlier is either a deviation greater than 20% from the study mean in the analysis of the injection standard or a deviation greater than two standard deviations in the analysis of the solid reference material.

TABLE 1			
Lab ID	Instances of deviations greater than 20% from the study mean (Injection standard)	Instances of deviations greater than two standard deviations (Reference standard MOE-PTSEC2)	Total incidences of outliers
98206	0	0	0
98208	0	1	1
98209	1	1	2
98211	1	2	3
98210	1	2	3
98207	4	1	5
98202	5	1	6
98203	4	7	11
98201	7	5	12
98204	11	4	15
98205	9	11	20

Overall, this study has identified some of the problems experienced by laboratories in the analysis of PAHs in solid materials, suggested solutions where ever possible and complemented the objectives of the training program in promoting the production of good quality analytical data in the province of Ontario.

2 INTRODUCTION

As an adjunct to the training program for Polynuclear Aromatic Hydrocarbons (PAH) in solid matrices conducted by the Laboratory Services Branch (LSB) of the Ontario Ministry of the Environment (MOE) in the fall of 1998, a Performance Assessment (PA) Program was offered to interested participants. The PA program was designed to:

- ▲ validate the instrument calibration
- ▲ assess the performance of the methodology
- ▲ provide opportunity for routine monitoring of the method.

Eight laboratories from the training program agreed to participate. Three other laboratories were invited to participate in this study.

Each laboratory was provided with three reference materials with detailed instructions for analysis. The three materials were:

- ▲ an injection ready reference standard in either acetonitrile or toluene (participating laboratory preference based on methodology used)
- ▲ A certified reference material - Lake sediment
- ▲ Another reference material - Lake sediment

Each participant was asked to analyze all three materials. Once received by the LSB the results were entered onto an electronic spreadsheet. A copy of the results spreadsheet was faxed to each participant to verify the accuracy of transcription.

3 RESULTS AND PERFORMANCE ASSESSMENT TECHNIQUES

3.1 Injection Standard MOE-PTS420/MOE-PTS426

This reference material was supplied by the National Water Research Institute (NWRI). The design value, medians of two interlaboratory studies and validation versus a commercial standard were provided to each participant along with the standard.

The results of the injection standard are presented in Table 2a, Table 2b and Table 2c (pages 9-11). The Dixon Outlier Test¹ was performed for each parameter and extreme results eliminated by this process are identified in red face in Table 2a. These outliers will greatly influence calculated means and standard deviations, especially if the data set is small and are therefore not used in the computation of means, SDs and CVs.

Results expressed as percentage of design value and study means are presented in Tables 2b and 2c respectively. In many instances the deviation of individual laboratory results from the design value or the study mean was greater than usually anticipated for calibration standards. As a starting point, those results that deviated greater than 20% from the design or study mean are identified in red face.

Laboratories are also ranked from low to high for each parameter. The laboratory with the lowest result for a parameter gets a rank of 1 for that parameter and the laboratory with the highest result for parameter gets a rank equal to the number of positive results reported for that parameter. Not all eleven laboratories reported results for all parameters. For example, results for naphthalene were reported by only ten laboratories.

As only five laboratories reported results for benzo(e)pyrene and perylene, these two parameters were excluded from this ranking exercise. The lowest possible average rank for a laboratory is 1 and the highest possible average rank for laboratory is close to 11. Laboratories whose average rank approaches such extreme values must suspect problems with their calibration standards for all the parameters. These extreme values indicate that the majority of the analytes in the laboratory's injection standard are either low or high in concentration compared to the study means which may suggest that the laboratory's mixed injection standard was incorrectly constituted from the primary individual standards or the mixed standard has deteriorated over a period of time. At any event, these laboratories must consider re-validating their calibration standards.

The ranks of individual laboratories are presented in Table 2d (page 12). Injection standard results are also presented in Figure 1 (page 18). The laboratories with the highest two and lowest two ranks are identified by lines joining individual points.

3.2 Reference Material MOE-PTSEC2

This is a certified reference material (EC2) also supplied by NWRI.

The results of the laboratories and the published certified values along with the uncertainty are presented in Table 3a (page 13), and Figures 2, 3 & 4 (pages 19- 21). The uncertainty represents

the standard deviation of a single measurement. Parameters identified with a superscript asterisk have only provisional values.

Assessment of individual laboratories is based on the published certified values and standard deviations for each parameter. Only parameters for which certified values are available are considered. In addition to 10 single parameters, a certified value is available for the combination of chrysene and triphenylene. All together, 11 parameters are assessed for each laboratory.

The performance of the laboratory for a parameter is considered satisfactory (S) if the deviation of the result of the laboratory is less than two standard deviations from the certified value. If the deviation of the result exceeds two standard deviation but less than three standard deviation, the laboratory is flagged as exceeding warning limits (W). If the deviation exceeds three standard deviation, the performance is flagged as out of control (OC).

The results of this assessment is presented on Table 3b (page 14)

3.3 Reference Material LSBRM9801

This is a lake sediment that is being developed as a certified reference material. At present there are no certified values.

The results of the laboratories are presented in Table 4a (page 15), and Figures 5, 6 & 7 (pages 22-24). The Dixon Outlier Test¹ was performed for each parameter and the corresponding means, SDs and CVs were computed for the data remaining after Dixon's elimination process. Eliminated data points are identified in red face in Table 4a. The results of the laboratories as a percentage of the study mean is presented in Table 4b (page 16).

The Reference Material LSBRM9801 was developed using ISO guidelines and produced in a facility certified to produce certified reference materials. The results of this study have shown that the PAH's are present in this material at very low levels, close to MDL's suggested in the Ministry's "Guidance on Sampling and Analytical Methods for use at Contaminated Sites in Ontario"². This fact, together with the tight distribution of results demonstrated by the participants as shown in Figures 5, 6 & 7, allow us to conclude that this material, LSBRM9801, would be a valuable QC Reference Material to be used routinely by laboratories to continuously monitor the performance of their method.

3.4 Graphical Review of Results of Solid Materials

The results of the two solid materials, namely Certified Reference Material MOE-PTSEC2 and Reference Material LSBRM9801, as expressed as a percentage of the study mean, are plotted one versus the other on a XY chart for each laboratory. Each point represents the pair of data of a single parameter. The graph is divided into four quadrants by two lines representing the mean result of each sample. As the results are expressed as a percentage of the study mean, these means dividing the graph correspond to 100%.

If no systematic errors are present, one would expect results to be equally distributed among the four quadrants as each of the following combinations will have the same probability of occurrence:

- high in MOE-PTSEC2, low in LSBRM9801 (lower right quadrant)
- high in MOE-PTSEC2, high in LSBRM9801 (upper right quadrant)
- low in MOE-PTSEC2, low in LSBRM9801 (lower left quadrant)
- low in MOE-PTSEC2, high in LSBRM9801 (upper left quadrant).

When the majority of the parameters are in the lower left quadrant and or upper right hand quadrants, it is reasonable to conclude that the laboratory is somewhat precise in their work but have a definite bias that may be due to problems associated with sample preparation/clean-up (poor recovery), and/or calibration. The majority of results in the upper left and lower right quadrants suggest precision problems which require more investigation to resolve.

The results of this assessment are provided in the individual assessment reports distributed along with this report.

4 OVERALL PERFORMANCE REVIEW

Individual assessment reports are provided for all participants laboratories along with recommendations for improvement. A typical report is provided in the appendix (page 27).

The study means of all but one of the parameters were not significantly different (at 95% confidence level) from the design value of the injection standard. However, the between laboratory variability is observed to be high as indicated by the study coefficient of variation for these parameters (Table 2a, page 9). For the purpose of this assessment, a deviation of 20% or less was arbitrarily chosen as the acceptance limit for satisfactory performance.

With the exception of Laboratory 98207, all the laboratories had results from one or more parameters that deviated greater than 20% of the design values of the injection standard. All the results of Laboratory 98206 and Laboratory 98208 were within 20% of the study mean. The rest of the laboratories had one or more the results that deviated greater than 20% from the study mean.

It is clear that most laboratories must re-validate their standards on a continuous basis.

Five laboratories namely 98202, 98206, 98207, 98208 and 98209 performed reasonably well in the analysis of the reference material MOE-PTSEC2 in that the result of only one parameter deviated from the certified value by more than two standard deviation. The rest of the laboratories had results of two or more parameters that deviated from the certified values by more than two standard deviations. The performance of laboratories 98201, 98203, 98204 and 98205 on the analysis of MOE-PTSEC2 must be considered not satisfactory.

The graphical review of data indicate that most laboratories are capable of precise analysis but are experiencing some systematic problems. In a few cases this may be related to the calibration standards. In others, it may be due to extraction deficiency. Clearly this one area where there is room for improvement.

The relative performance of the laboratories are assessed on the basis of number of outliers. An outlier is either a deviation greater than 20% from the study mean in the analysis of the injection standard or a deviation greater than two standard deviations in the analysis of the solid reference material. The results of this assessment is presented in Table 1 (page 2)

The performance of Laboratory 98206 is outstanding. All parameters of the injection standards were within 20% of the study mean and in the analysis of the reference material MOE-PTSEC2, no parameter deviated from the certified value by more than two standard deviations.

Second to Laboratory 98206 is Laboratory 98208. All parameters of the injection standards were within 20% of the study mean and only one parameter in the analysis of the reference material MOE-PTSEC2, deviated from the certified value by more than two standard deviations.

Overall, this study has identified some of the problems experienced by laboratories in the analysis of PAHs in solid materials, suggested solutions where ever possible and complemented the

objectives of the training program in promoting the production of good quality analytical data in the province of Ontario.

5 METHODOLOGY SUMMARY

A brief summary of methodology used by the various laboratories is presented on Table 5 (page 17).

All the laboratories employed GC/MS methodology for the instrumental analysis. The stationary phase of the columns used by the majority of the laboratories are very much similar.

Two laboratories indicated that the solid materials were dried with either magnesium sulphate or sodium sulphate prior to extraction. One indicated that the solid materials were not dried prior to extraction. Others did not indicate whether samples were dried or not prior to extraction.

Laboratory 98201 did not indicate the extraction procedure. Seven laboratories used sonification. Three laboratories used soxhlet extraction. Laboratory 98209 reported results using two extraction procedures namely soxhlet extraction and microwave assisted process (MAP). A plot of soxhlet results versus MAP results of Laboratory 98209 (Figure 8, page 25) shows that the latter tends to produce slightly lower results.

Six laboratories used some kind of clean-up procedure after extraction. Four among these used silica. One used alumina and the other used copper. Three laboratories indicated that they did not perform a clean up after extraction.

All laboratories employed one or more surrogates as means of monitoring sample processing efficiency. But, no laboratory corrected the final results based on surrogate recovery.

6 BIBLIOGRAPHY

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2. Guidance on Sampling and Analytical Methods for use at Contaminated Sites in Ontario, Queen's printer for Ontario, 1996, ISBN-0-7778-5908-4.

7 TABLES AND FIGURES

TABLE 2a: Results of Injection Standard in µg/mL

Parameter	Design value	98201	98202	98203	98204	98205	98206	98207	98208	98209	98210	98211	mean	sd	cv	n
acenaphthene	0.4722	0.51	0.423	0.480	0.417	0.528	0.473	0.460	0.420	0.444	0.463	0.470	0.463	0.034	7%	11
acenaphthylene	0.4933	0.483	0.351	0.407	0.360	0.433	0.425	0.417	0.400	0.332	0.397	0.383	0.399	0.040	10%	11
anthracene	0.09736	0.117	0.068	0.083	0.080	0.086	0.085	0.106	0.090	0.076	0.067	0.080	0.085	0.014	17%	11
benzo(a)anthracene	0.24	0.547	0.193	0.310	0.250	0.345	0.267	0.257	0.200	0.220	0.210	0.220	0.247	0.047	19%	10
benzo(a)pyrene	0.4844	0.540	0.373	0.520	0.320	0.591	0.483	0.438	0.387	0.426	0.450	0.427	0.450	0.075	17%	11
benzo(b)fluoranthene	0.5709	0.523	0.394	0.570	0.323	0.674	0.555	0.621	0.440	0.488	0.500	0.533	0.511	0.095	19%	11
benzo(e)pyrene	0.4961		0.384			0.693		0.463		0.461		0.537	0.461	0.054	12%	4
benzo(g,h,i)perylene	0.4367	0.667	0.576	0.557	0.317	0.546	0.512	0.469	0.470	0.499	0.530	0.410	0.505	0.087	17%	11
benzo(k)fluoranthene	0.3639	0.197	0.246	0.350	0.173	0.371	0.312	0.338	0.280	0.233	0.283	0.270	0.278	0.060	22%	11
chrysene	0.7679	0.687	0.491	0.610	0.390	0.701	0.628	0.644	0.520	0.480	0.630	0.540	0.575	0.093	16%	11
dibenzo(a,h)anthracene	0.09871	0.120	0.054	0.170	0.047	0.081	0.084	0.099	0.060	0.073	0.063	0.063	0.074	0.021	28%	10
fluoranthene	0.9764	1.027	0.828	0.827	0.520	1.059	0.933	0.954	0.877	0.815	0.863	0.813	0.865	0.136	16%	11
fluorene	0.4731	0.473	0.393	0.413	0.287	0.509	0.437	0.432	0.400	0.436	0.457	0.433	0.425	0.054	13%	11
indeno(1,2,3-c,d)pyrene	0.4906	0.583	0.338	0.660	0.313	0.499	0.356	0.474	0.443	0.377	0.363	0.287	0.427	0.112	26%	11
naphthalene	0.4972	0.570	0.397	0.547	0.483	0.518	0.488	0.492	0.447		0.473	0.440	0.485	0.049	10%	10
perylene	0.1977		0.120			0.308		0.217		0.133		0.230	0.202	0.069	34%	5
phenanthrene	0.5016	0.517	0.370	0.373	0.297	0.502	0.470	0.456	0.420	0.467	0.500	0.433	0.437	0.064	15%	11
pyrene	0.9827	0.987	0.898	0.887	0.553	1.121	0.911	1.013	0.933	0.789	0.780	0.927	0.891	0.140	16%	11

NOTE: Results high lighted in red face were identified as outliers by the Dixon Test.

TABLE 2b: Results of Injection Standard Expressed as Percentage of Design Value

Parameter	98201	98202	98203	98204	98205	98206	98207	98208	98209	98210	98211
acenaphthene	108%	90%	102%	88%	112%	100%	97%	89%	94%	98%	100%
acenaphthylene	98%	71%	82%	73%	88%	86%	85%	81%	67%	80%	78%
anthracene	120%	70%	86%	82%	88%	87%	109%	92%	78%	68%	82%
benzo(a)anthracene	228%	81%	129%	104%	144%	111%	107%	83%	92%	88%	92%
benzo(a)pyrene	111%	77%	107%	66%	122%	100%	90%	80%	88%	93%	88%
benzo(b)fluoranthene	92%	69%	100%	57%	118%	97%	109%	77%	86%	88%	93%
benzo(e)pyrene		77%			140%		93%		93%		108%
benzo(g,h,i)perylene	153%	132%	127%	73%	125%	117%	107%	108%	114%	121%	94%
benzo(k)fluoranthene	54%	68%	96%	48%	102%	86%	93%	77%	64%	78%	74%
chrysene	89%	64%	79%	51%	91%	82%	84%	68%	62%	82%	70%
dibenzo(a,h)anthracene	122%	54%	172%	47%	82%	85%	100%	61%	74%	64%	64%
fluoranthene	105%	85%	85%	53%	108%	96%	98%	90%	84%	88%	83%
fluorene	100%	83%	87%	61%	108%	92%	91%	85%	92%	97%	92%
indeno(1,2,3-c,d)pyrene	119%	69%	135%	64%	102%	73%	97%	90%	77%	74%	58%
naphthalene	115%	80%	110%	97%	104%	98%	99%	90%		95%	88%
perylene		61%			156%		110%		67%		116%
phenanthrene	103%	74%	74%	59%	100%	94%	91%	84%	93%	100%	86%
pyrene	100%	91%	90%	56%	114%	93%	103%	95%	80%	79%	94%

TABLE 2c: Results of Injection Standard Expressed as Percentage of Study Mean

Parameter	98201	98202	98203	98204	98205	98206	98207	98208	98209	98210	98211
acenaphthene	110%	92%	104%	90%	114%	102%	99%	91%	96%	100%	102%
acenaphthylene	121%	88%	102%	90%	109%	107%	105%	100%	83%	99%	96%
anthracene	137%	80%	98%	94%	101%	100%	124%	106%	89%	78%	94%
benzo(a)anthracene	221%	78%	125%	101%	140%	108%	104%	81%	89%	85%	89%
benzo(a)pyrene	120%	83%	115%	71%	131%	107%	97%	86%	95%	100%	95%
benzo(b)fluoranthene	102%	77%	112%	63%	132%	109%	122%	86%	96%	98%	104%
benzo(e)pyrene	.	83%			150%		100%		100%		116%
benzo(g,h,i)perylene	132%	114%	110%	63%	108%	102%	93%	93%	99%	105%	81%
benzo(k)fluoranthene	71%	89%	126%	62%	134%	112%	122%	101%	84%	102%	97%
chrysene	119%	86%	106%	68%	122%	109%	112%	90%	83%	110%	94%
dibenzo(a,h)anthracene	162%	72%	229%	63%	109%	113%	133%	81%	98%	85%	85%
fluoranthene	119%	96%	96%	60%	122%	108%	110%	101%	94%	100%	94%
fluorene	111%	93%	97%	68%	120%	103%	102%	94%	103%	108%	102%
indeno(1,2,3-c,d)pyrene	137%	79%	155%	73%	117%	83%	111%	104%	88%	85%	67%
naphthalene	117%	82%	113%	100%	107%	100%	101%	92%		97%	91%
perylene	.	60%			153%		108%		66%		114%
phenanthrene	118%	85%	85%	68%	115%	108%	104%	96%	107%	114%	99%
pyrene	111%	101%	100%	62%	126%	102%	114%	105%	89%	88%	104%

TABLE 2d: Ranking Order

Parameter	98201	98202	98203	98204	98205	98206	98207	98208	98209	98210	98211
acenaphthene	10	3	9	1	11	8	5	2	4	6	7
acenaphthylene	11	2	7	3	10	9	8	6	1	5	4
anthracene	11	2	6	5	8	7	10	9	3	1	4
benzo(a)anthracene	11	1	9	6	10	8	7	2	4	3	5
benzo(a)pyrene	10	2	9	1	11	8	6	3	4	7	5
benzo(b)fluoranthene	6	2	9	1	11	8	10	3	4	5	7
benzo(g,h,i)perylene	11	10	9	1	8	6	3	4	5	7	2
benzo(k)fluoranthene	2	4	10	1	11	8	9	6	3	7	5
chrysene	10	3	6	1	11	7	9	4	2	8	5
dibenzo(a,h)anthracene	10	2	11	1	7	8	9	3	6	4	5
fluoranthene	10	5	4	1	11	8	9	7	3	6	2
fluorene	10	2	4	1	11	8	5	3	7	9	6
indeno(1,2,3-c,d)pyrene	10	3	11	2	9	4	8	7	6	5	1
naphthalene	10	1	9	5	8	6	7	3		4	2
phenanthrene	11	2	3	1	10	8	6	4	7	9	5
pyrene	9	5	4	1	11	6	10	8	3	2	7
AVERAGE RANK	9.5	3.1	7.5	2.0	9.9	7.3	7.6	4.6	4.1	5.5	4.5

TABLE 3a: Results of MOE-PTSEC2 (µg/mL)

Parameter	Certified Value	98201	98201	98203	98204	98205	98206	98207	98208	98209	98210	98211	98209a
Acenaphthene*	0.2 ± 0.04	0.04	<.2	0.03	0.062	0.00856	0.039	0.05	0.02	0.02	0.05	0.03	0.023
Acenaphthylene*	0.12 ± 0.02	0.13	0.301	0.16	0.227	0.02255	0.364	0.26	0.24	0.067	0.65	0.59	0.059
anthanthrene										0.172		0.19	0.254
Anthracene*	0.11 ± 0.02	0.07	0.267	0.55	0.257	0.04059	0.113	0.14	0.15	0.388	0.36	0.29	0.45
benzo(a)anthracene	1.42 ± 0.25	0.46	1.04	2.33	0.977	0.16091	0.954	0.92	0.96	0.855	1.4	0.18	1.044
benzo(a)pyrene	1.21 ± 0.28	0.68	1.04	1.95	1.33	0.18082	0.955	0.88	0.77	0.789	1	1	1.103
benzo(b)fluoranthene	2.48 ± 0.43	1.87	2.37	4.92	2.794	0.43791	1.89	2.69	2.35	2.74	2.3	3	3.406
benzo(e)pyrene	1.91 ± 0.36		1.64			0.1693		1.65		1.429		1.7	1.815
benzo(g,h,i)perylene	1.47 ± 0.33	0.7	1.25	3.28	1.671	0.22221	1.13	1.4	0.99	1.008	0.47	1.2	1.37
benzo(k)fluoranthene	1.93 ± 0.36	1.22	2.25	1.74	4.403	0.16025	2.11	2.15	1.55	1.481	2.2	1.8	1.929
chrysene		1.68	2.43	2.49	3.6	0.26492	2.14	2.47	1.75	1.694	2.1	0.02	2.333
dibenzo(a,h)anthracene	0.49 ± 0.10	0.23	0.466	2.4	0.609	0.11736	0.517	0.54	0.67	0.406	0.37	0.49	0.568
fluoranthene	3.55 ± 0.41	2.62	4.24	3.59	6.78	0.32457	3.27	3.98	3.6	3.29	3.7	3.5	4.162
fluorene*	2.14 ± 0.40	0.81	<.2	0.69	0.107	0.02642	0.056	0.33	0.05	0.037	1	0.93	0.05
indeno(1,2,3-c,d)pyrene	1.55 ± 0.26	1.14	2.21	2.94	2.6	0.34624	1.78	1.98	2.64	1.47	0.97	2	2.03
naphthalene*	1.47 ± 1.05	1.9	5.37	2.25	3.38	0.0345	2.1	1.89	2		4.2	6.2	
perylene*	0.80 ± 0.26		0.452			0.26486		0.31		0.361		0.43	0.427
phenanthrene*	1.41 ± 0.16	1.5	1.5	1.63	4.01	0.17384	1.2	1.93	1.68	1.319	1.3	1.7	1.716
pyrene	2.92 ± 0.31	2.26	3.05	3.6	5.04	0.22399	2.53	2.89	2.74	2.484	3.2	3.2	3.152
triphenylene										0.405			0.557
triphenylene + chrysene	2.15 ± 0.86	1.68	2.43	2.49	3.6	.265	2.14	2.47	1.75	2.09	2.1	0.02	2.89

* Values provided under the certified column are provisional values
Uncertainty represents the standard deviation of a single measurement

TABLE 3b: Performance Assessment

Parameter	98201	98202	98203	98204	98205	98206	98207	98208	98209	98210	98211	98209a
benzo(a)anthracene	OC	S	OC	S	OC	S	W	S	W	S	OC	S
benzo(a)pyrene	S	S	W	S	OC	S	S	S	S	S	S	S
benzo(b)fluoranthene	S	S	OC	S	OC	S	S	S	S	S	S	W
benzo(e)pyrene		S			OC		S		S		S	S
benzo(g,h,i)perylene	W	S	OC	S	OC	S	S	S	S	OC	S	S
benzo(k)fluoranthene	S	S	S	OC	OC	S	S	S	S	S	S	S
dibenzo(a,h)anthracene	W	S	OC	S	OC	S	S	S	S	S	S	S
fluoranthene	W	S	S	OC	OC	S	S	S	S	S	S	S
indeno(1,2,3-c,d)pyrene	S	W	OC	OC	OC	S	S	OC	S	W	S	S
pyrene	W	S	W	OC	OC	S	S	S	S	S	S	S
triphenylene/chrysene	S	S	S	S	W	S	S	S	S	S	W	S

S = Satisfactory Performance (deviation from certified value is less than 2 standard deviation)

W = Warning (deviation from certified value is between 2 and 3 standard deviation)

OC=Out of Control (deviation from certified value is greater than 3 standard deviation)

TABLE 4a: Results of Reference Material LSBRM9801 in µg/g

Parameter	98201	98202	98203	98204	98205	98206	98207	98208	98209	98210	98211	98209A	mean	sd	cv	n
acenaphthene	0.02	<0.02	<.01	0.011	0.021	<.01	0.01		0.009	<.05	<.01	0.006	0.013	0.006	46%	6
acenaphthylene	0.02	<0.02	<.01	0.016	0.217	<.015	<.08	0.01	0.004	<.05	0.03	0.006	0.014	0.009	64%	6
anthanthrene									0.013		0.01	0.017	0.013	0.003	23%	3
anthracene	0.04	0.037	0.07	0.029	0.069	0.015	0.01	0.02	0.02	<.05	0.03	0.019	0.033	0.019	58%	11
benzo(a)anthracene	0.08	0.118	0.12	0.096	0.484	0.066	<.05	0.09	0.083	0.11	0.1	0.091	0.095	0.016	17%	10
benzo(a)pyrene	0.11	0.17	0.18	0.207	0.490	0.108	<.17	0.11	0.132	0.14	0.16	0.168	0.149	0.032	21%	10
benzo(b)fluoranthene	0.12	0.271	0.36	0.381	1.797	0.155	<.17	0.25	0.303	0.21	0.36	0.329	0.274	0.085	31%	10
benzo(e)pyrene		0.189			0.530		<.05		0.167		0.21	0.192	0.19	0.015	8%	4
benzo(g,h,i)perylene	0.14	0.159	0.08	0.36	0.658	0.113	<.36	0.12	0.133	0.07	0.12	0.171	0.123	0.031	25%	9
benzo(k)fluoranthene	0.08	0.234	0.11	0.248	0.689	0.143	<.25	0.14	0.167	0.17	0.19	0.329	0.181	0.069	38%	10
chrysene	0.11	0.245	0.1	0.309	1.139	0.139	<.05	0.15	0.152	0.15	0.21	0.176	0.174	0.061	35%	10
dibenzo(a,h)anthracene	0.02	0.063	0.18	0.085	0.177	0.035	<.01	0.07	0.042	<.05	0.07	0.055	0.08	0.053	66%	10
fluoranthene	0.27	0.414	1.22	1.45	1.683	0.189	<.05	0.22	0.311	0.16	0.27	0.298	0.59	0.54	92%	10
fluorene	0.03	<0.02	<.01	0.044	0.423	0.012	0.01	0.01	0.017	<.05	0.03	0.016	0.021	0.011	52%	8
indeno(1,2,3-c,d)pyrene	0.16	0.312	0.26	0.4	1.084	0.162	<.23	0.28	0.202	0.14	0.21	0.256	0.238	0.076	32%	10
naphthalene	0.06	0.042	0.02	0.048	1.424	0.02	0.02	0.04		<.05	0.05		0.038	0.015	39%	8
perylene		0.262			0.152		<.1		0.211		0.21	0.235	0.214	0.036	17%	5
phenanthrene	0.11	0.157	0.24	0.262	0.694	0.092	0.04	0.11	0.142	0.12	0.16	0.138	0.119	0.035	29%	9
pyrene	0.14	0.25	0.19	0.47	1.238	0.169	<.06	0.17	0.224	0.2	0.26	0.298	0.211	0.048	23%	9
triphenylene									0.054			0.059	0.057	0.003	5%	5

NOTE: Results high lighted in red face were identified as outliers by the Dixon Test.

TABLE 4b: Results of Reference Material LSBRM9801 Expressed as Percentage of Study Mean

Parameter	98201	98202	98203	98204	98205	98206	98207	98208	98209	98210	98211	98209a
acenaphthene	154%			85%	159%		77%		69%			46%
acenaphthylene	143%			114%	1553%			71%	29%		214%	43%
anthanthrene									100%		77%	131%
anthracene	121%	112%	212%	88%	209%	45%	30%	61%	61%		91%	58%
benzo(a)anthracene	84%	124%	126%	101%	510%	69%		95%	87%	116%	105%	96%
benzo(a)pyrene	74%	114%	121%	139%	329%	72%		74%	89%	94%	107%	113%
benzo(b)fluoranthene	44%	99%	131%	139%	656%	57%		91%	111%	77%	131%	120%
benzo(e)pyrene		99%			279%				88%		111%	101%
benzo(g,h,i)perylene	114%	129%	65%	293%	535%	92%		98%	108%	57%	98%	139%
benzo(k)fluoranthene	44%	129%	61%	137%	381%	79%		77%	92%	94%	105%	182%
chrysene	63%	141%	57%	178%	654%	80%		86%	87%	86%	121%	101%
dibenzo(a,h)anthracene	25%	79%	225%	106%	222%	44%		88%	53%	0%	88%	69%
fluoranthene	46%	70%	207%	246%	285%	32%		37%	53%	27%	46%	51%
fluorene	143%			210%	2012%	57%	48%	48%	81%		143%	76%
indeno(1,2,3-c,d)pyrene	67%	131%	109%	168%	456%	68%		118%	85%	59%	88%	108%
naphthalene	158%	111%	53%	126%	3747%	53%	53%	105%			132%	
perylene		122%			71%				99%		98%	110%
phenanthrene	92%	132%	202%	220%	584%	77%	34%	92%	119%	101%	134%	116%
pyrene	66%	118%	90%	223%	587%	80%		81%	106%	95%	123%	141%

TABLE 5: Methodology Summary

Lab Code	Sample Processing						Instrumental Conditions		
	Sample size	Drying prior to extraction	Extraction solvent	Extraction process	clean-up	Surrogate Recovery correction	Column	Detector	solvent
98201	NI	NI	DCM/acetone	NI	no	no	DB-5	saturn2000/ion trap	Hexane
98202	NI	NI	DCM	Soxhlet	alumina	no	HP-5MS	GC/MS	Toluene
98203	2-5g	NI	DCM	sonification	copper cleanup for LSB9801 only	no	DB-XLB	GC/MS	DCM
98204	10g	NI	DCM	sonification	no	no	HP-5	GC/MS	Hexane
98205	10g	no	acetone/hexane	sonification	no	no	DB-5.625	GC?	DCM
98206	NI	with MgSO ₄	acetone/hexane	sonification	NI	no	DB-5	GC/MS	Toluene
98207	NI	NI		sonification	Hg/silica	no	DB-5	GC/MS	Iso-octane
98208	NI	NI	acetone/hexane	sonification	silica	no	RTX-5	GC/MS	Toluene
98209	NI	NI	acetone/hexane	MAP	silica	no	DB-XLB	GC/MS	Toluene
98209a	NI	NI	DCM	Soxhlet	silica	no	DB-XLB	GC/MS	Toluene
98210	NI	NI	DCM/acetone	sonification & shake	NI	no	RH 5	GC/MS	DCM
98211	NI	with Na ₂ SO ₄	DCM	Soxhlet	NI	no	DB-5	GC/MS	Toluene

NI No information
MAP Microwave assisted process

FIGURE 1: PAH STUDY 9802
INJECTION STANDARD RESULTS

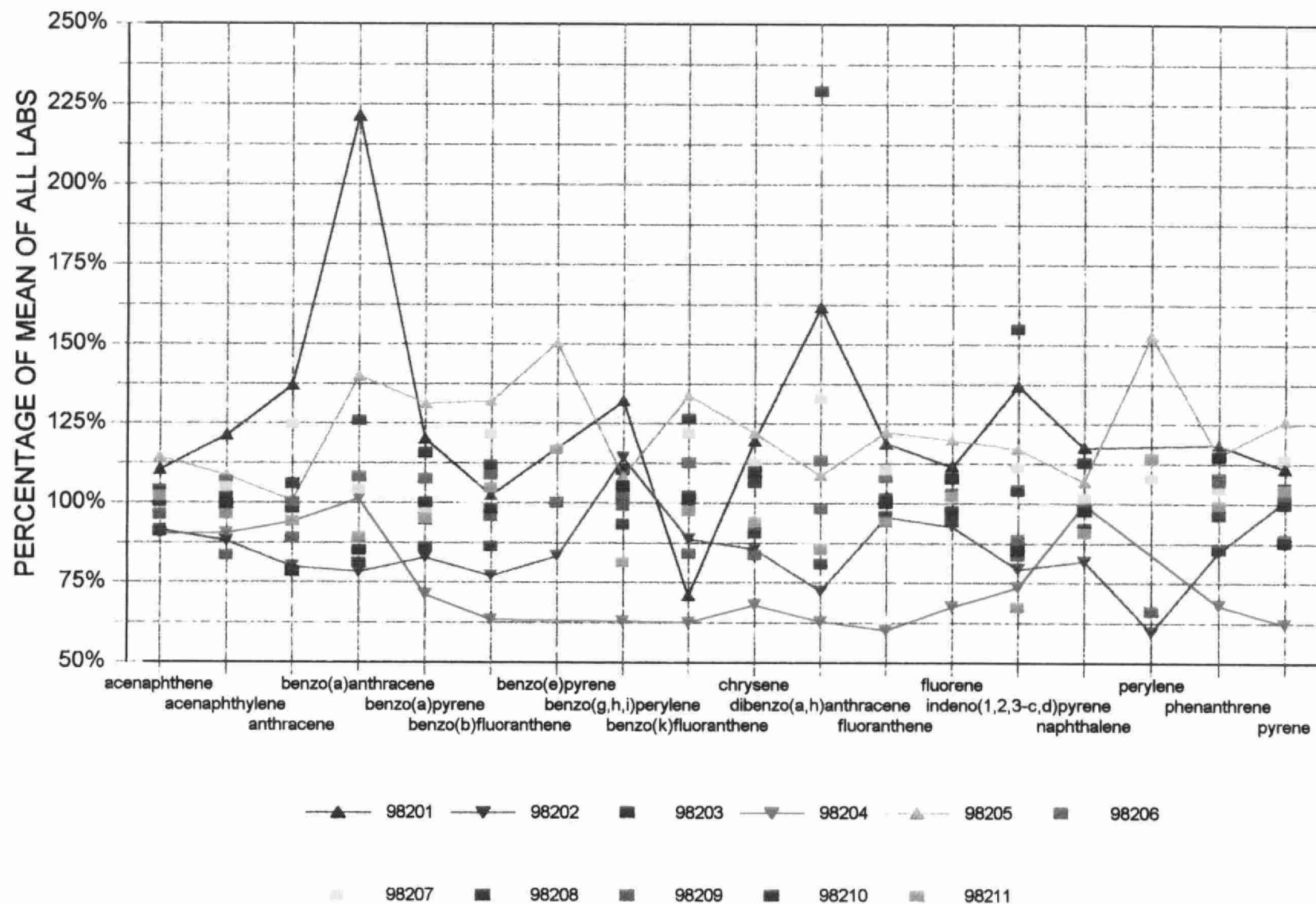
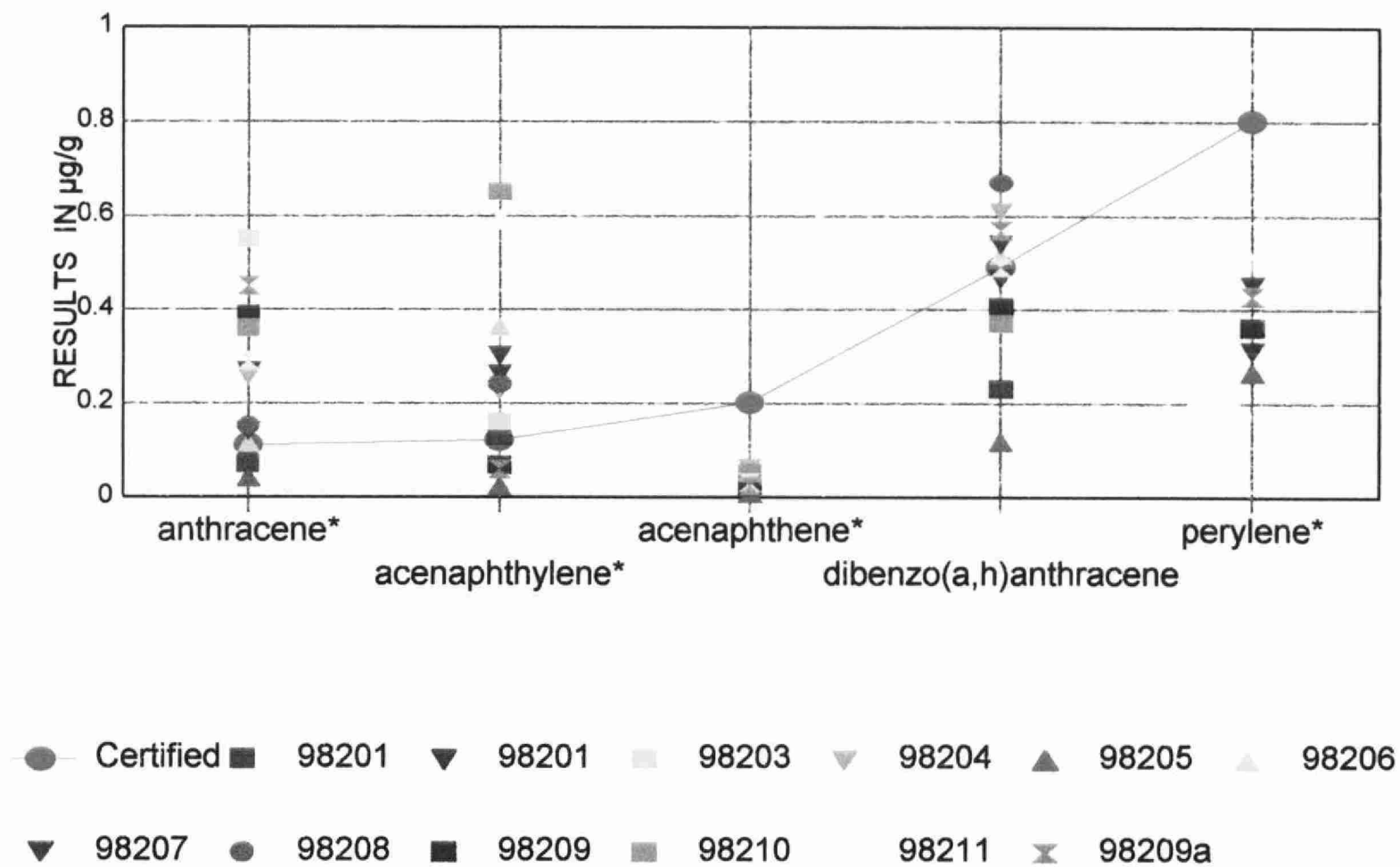
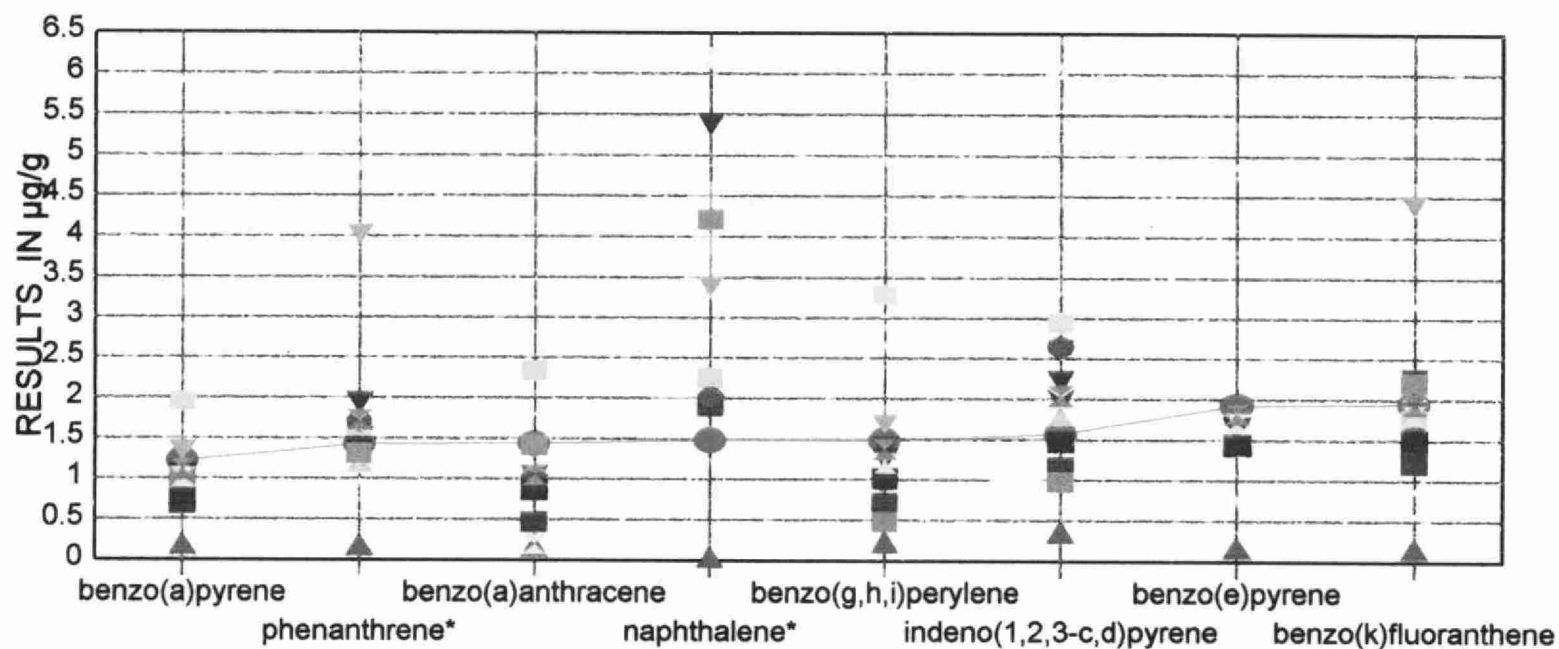


FIGURE 2: RESULTS OF MOE-PTSEC2



* Provisional certified values

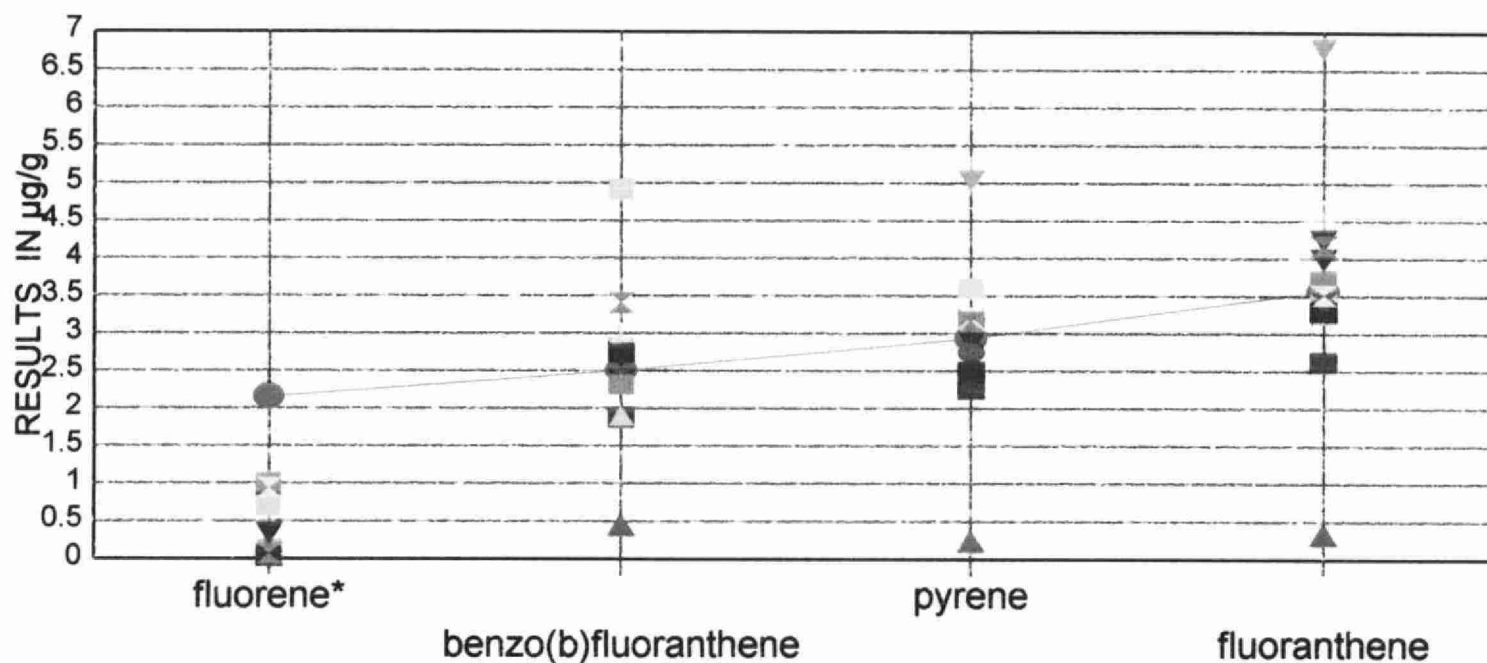
FIGURE 3: RESULTS OF MOE-PTSEC2



Certified 98201 98201 98203 98204 98205 98206
 98207 98208 98209 98210 98211 98209a

* Provisional certified values

FIGURE 4: RESULTS OF MOE-PTSEC2



Certified 98201 98201 98203 98204 98205 98206
 98207 98208 98209 98210 98211 98209a

* Provisional certified values

FIGURE 5: RESULTS OF LSBRM9801

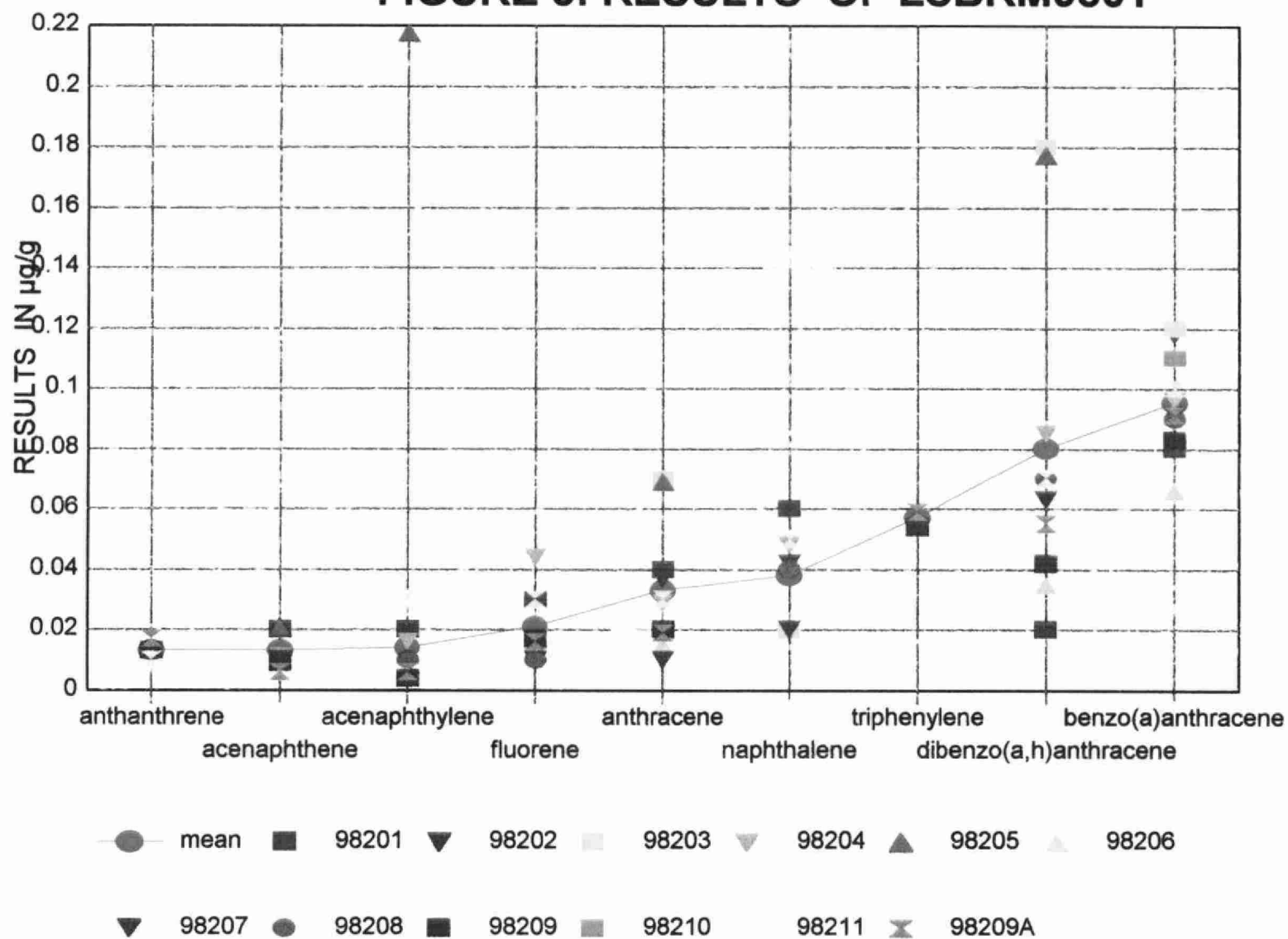


FIGURE 6: RESULTS OF LSBRM9801

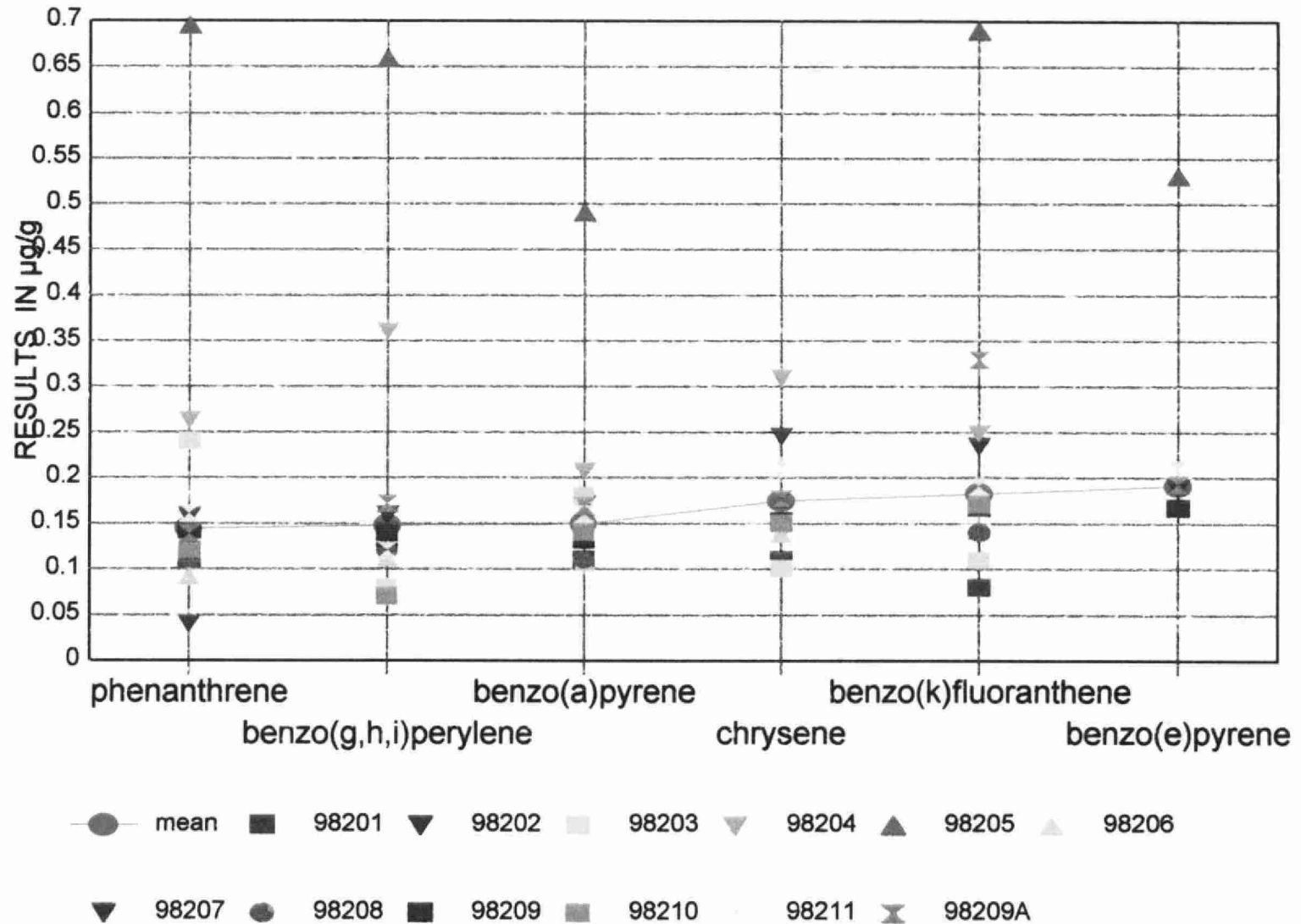


FIGURE 7: RESULTS OF LSBRM9801

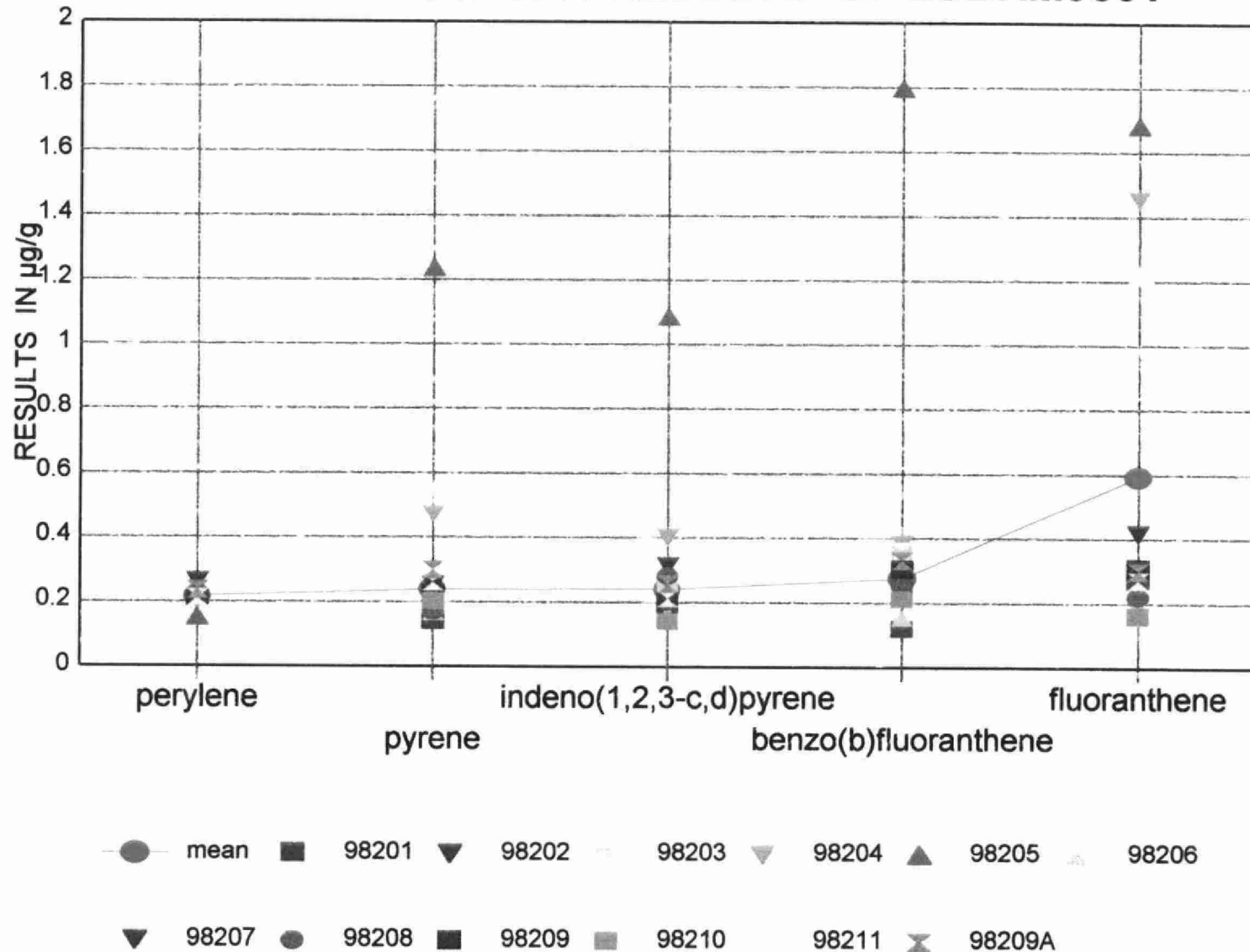
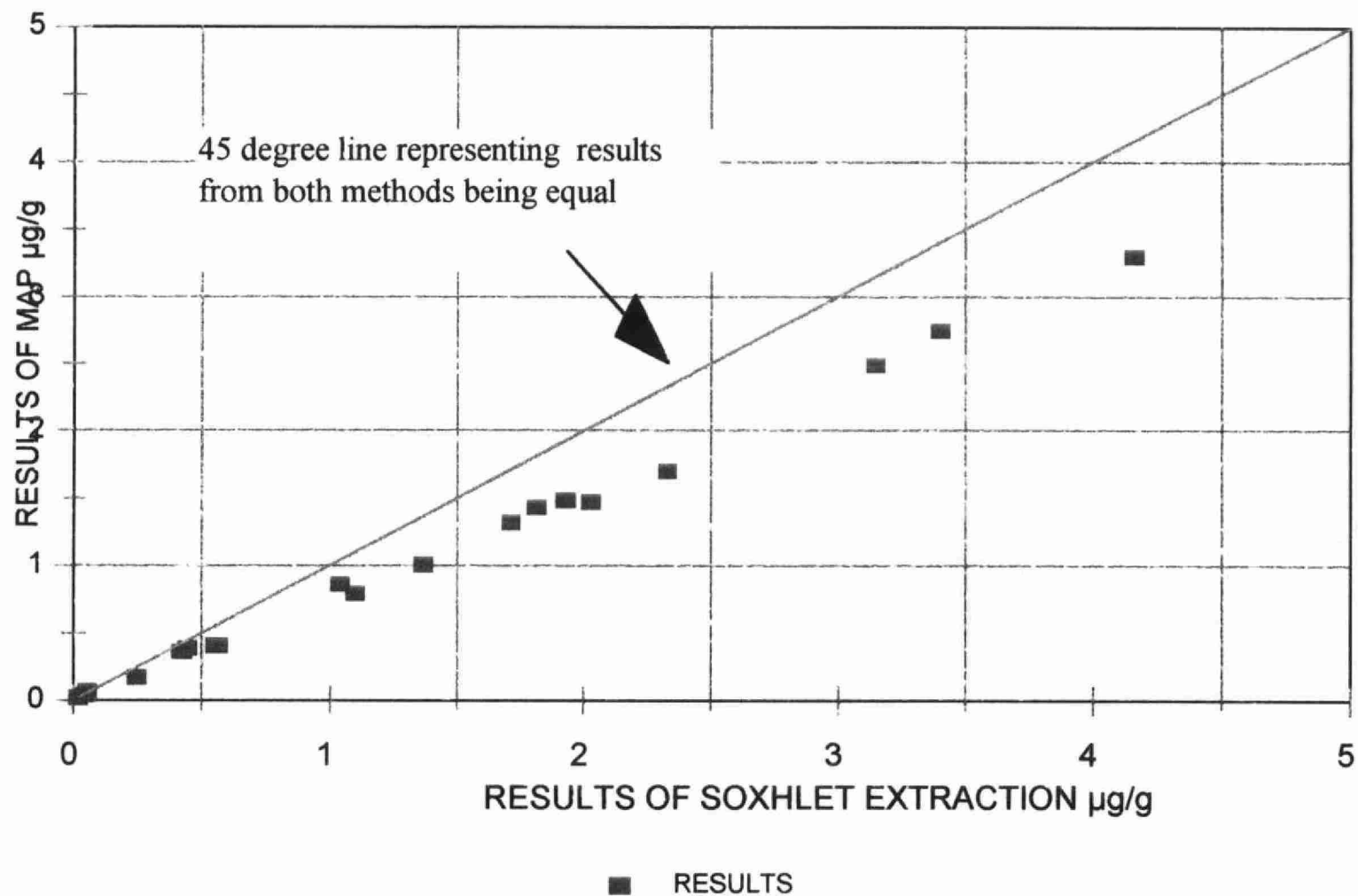


FIGURE 8: LABORATORY 98209
RESULTS OF TWO EXTRACTION PROCESS



8 LIST OF PARTICIPANTS

Laboratory

Accutest Laboratories Ltd.

Agra Earth and Environmental

Entech Laboratories

Environment Canada, Analysis and Air Quality Division, Ottawa

Envirotest Laboratories, Alberta

Envirotest Laboratories, Manitoba

Ontario Ministry of the Environment, Laboratory Services Branch

Maxxam Analytics Inc., Mississauga

Maxxam Analytics Inc., Waterloo

National Laboratory for Environmental Testing, Burlington

Philip Analytical Services Corporation, Burlington

9 APPENDIX - EXAMPLE OF INDIVIDUAL PERFORMANCE ASSESSMENT

POLYNUCLEAR AROMATIC HYDROCARBONS IN SOLID MATRICES

Interlaboratory Study 98-2

PERFORMANCE ASSESSMENT OF LABORATORY XXXXX

Injection standard: The laboratory reported results for sixteen parameters, of which only four parameters, namely acenaphthene, anthracene, benzo(a)anthracene and naphthalene were within 20% of the design (see Tables 1a, 1b, 1c). The results of the rest were all below 80% of the design value. Eleven parameters were below 80% of the study mean as well.

In general the results of this laboratory tends to be lower than the rest as demonstrated by the ranking procedure described below (see Table 1d and Figure 1).

Laboratories are ranked from low to high for each parameter. The laboratory with the lowest result for a parameter gets a rank of 1 for that parameter and the laboratory with the highest result for parameter gets a rank equal to the number of positive results reported for that parameter.

The average rank for this laboratory is 2.0

Certified Reference Material MOE-PTSEC2

This laboratory reported results for ten of the eleven parameters certified. Six parameters were within two standard deviation of the certified value (identified by "S" on Table 2b.). The deviation of the rest exceeded three standard deviations and hence flagged as out of control (OC) in Table 3b.

In general, the performance of this laboratory on this material must be considered not satisfactory.

Reference Material LSBRM9801

There are no certified values for this material. Based on results as percentage of study mean, the performance of this laboratory must be considered satisfactory for most parameters considering that the analytes are present at very low levels close to the MDLs suggested in the Ministry's Guidance on Sampling and Analytical Methods for use at Contaminated Sites in Ontario.

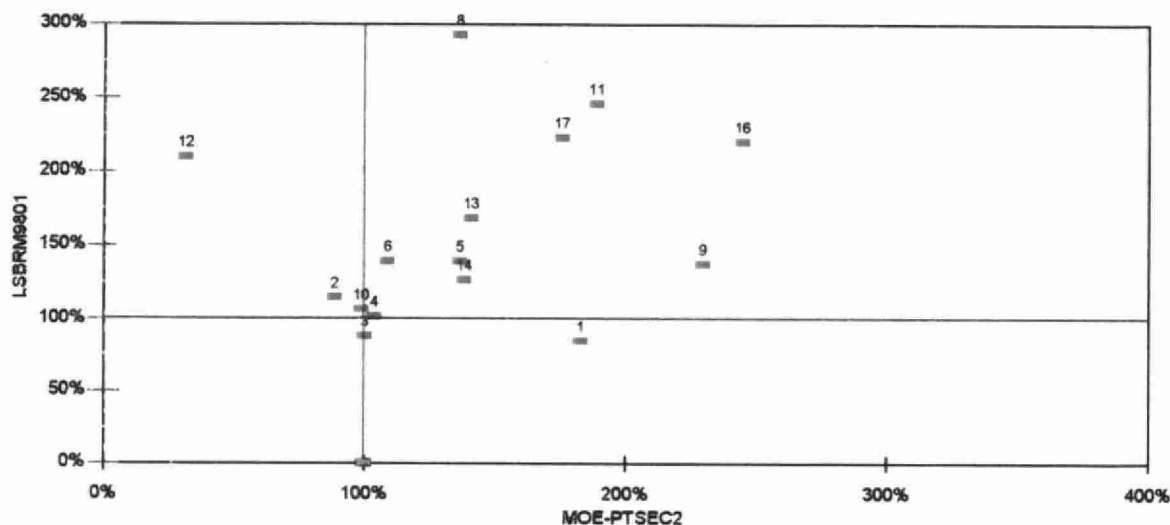
Graphical Review

This laboratory's results of the two solid materials, namely Certified Reference Material MOE-PTSEC2 and Reference Material LSBRM9801, as expressed as percentage of the study mean are plotted one versus the other on a XY chart (see Figure 9). The majority of the parameters are

POLYNUCLEAR AROMATIC HYDROCARBONS IN SOLID MATRICES

Interlaboratory Study 98-2

FIGURE 9: LABORATORY XXXXX



either in the lower left quadrant or upper right quadrant which indicates that this laboratory is capable of producing precise results most of the time, but demonstrates a definite high bias for most parameters.

Recommendation

It is recommended that the calibration standards be re-validated.

It is also recommended that a reference material be used routinely to monitor the performance of this method.

- 1 Acenaphthene
- 2 Acenaphthylene
- 3 Acenaphthene
- 4 benzo(a)anthracene
- 5 benzo(a)pyrene
- 6 benzo(b)fluoranthene
- 7 benzo(e)pyrene
- 8 benzo(g,h,i)perylene
- 9 benzo(k)fluoranthene
- 10 dibenzo(a,h)anthracene
- 11 fluoranthene
- 12 fluorene
- 13 indeno(1,2,3-c,d)pyrene
- 14 naphthalene
- 15 perylene
- 16 phenanthrene
- 17 pyrene

MOE/POL/AIXM
Cussion, Sylvia
Polynuclear aromatic
hydrocarbons in aixm
c.1 a aa



(8027)
MOE/POL/AIXM